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Short Communication

THERMAL DECOMPOSITION OF HYDROXYLAMMONIUM NEODYMIUM SULFATE DIHYDRATE

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The thermal decomposition of hydroxylammonium neodymium sulfate dihydrate has been investigated by simultaneous thermogravimetry and differential thermal analysis. Chemical analysis, X-ray powder spectra and infrared spectroscopy have been employed to characterize the intermediates and the final product. The thermal decomposition can be described by the sequence

$$(NH_3OH)Nd(SO_4)_2 \cdot 2\,H_2O \rightarrow (NH_3OH)Nd(SO_4)_2 \rightarrow$$
$$\rightarrow NH_4Nd_3(SO_4)_5 \rightarrow Nd_2(SO_4)_3.$$

The first and the second reactions overlap, but the last one is well separated from the first two.

Studies on the thermal decomposition of hydroxylammonium compounds are scarce. NH_2OH is known to decompose above 100° according to $3\,NH_2OH = NH_3 + N_2 + 3\,H_2O$ [1].

Similarly, $(NH_3OH)Cl$ decomposes above 157° as follows: $3\,(NH_3OH)Cl = NH_4Cl + 2\,HCl + N_2 + 3\,H_2O$ [2].

In the case of $(NH_3OH)_2SO_4$ two stages have been observed. The first is an exothermal loss of NH_2OH, and the second the evaporation of H_2SO_4 [3].

Experimental

The compound $(NH_3OH)Nd(SO_4)_2 \cdot 2\,H_2O$ was prepared from aqueous solutions of the two sulfates. The composition was proved by elemental analysis and by single-crystal structure analysis [4].

The simultaneous TG and DTA measurements were performed with a Mettler thermoanalyzer in a dynamic air atmosphere at a flow rate of 30 ml min^{-1}. Measure-

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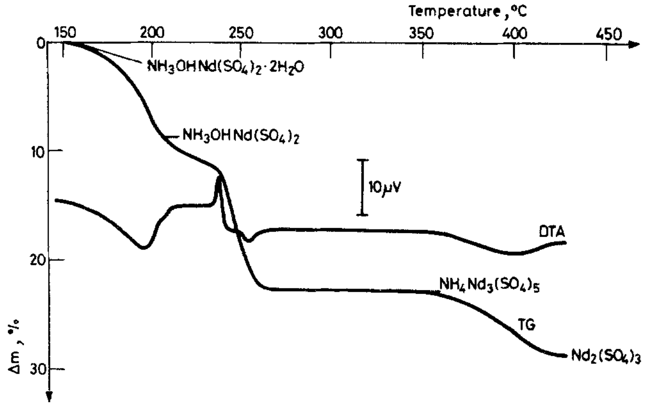

Fig. 1 TG and DTA curves of $(NH_3OH)Nd(SO_4)_2 \cdot 2\,H_2O$

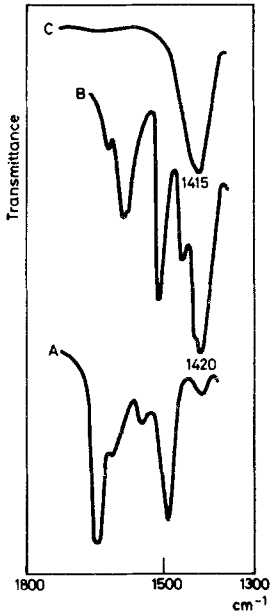

Fig. 2 IR spectra of initial (A) and intermediate phases (B: 15.6% mass loss, C: 23% mass loss)

ments were carried out in Pt crucibles at a heating rate of 2 deg · min^{-1}, with a sample mass of 20 mg. Inert alumina was used as reference material for DTA. Intermediate phases were obtained by heating the initial compound at a rate of 2 deg · min^{-1} to the desired temperature and cooling down the samples.

Table 1 X-ray powder data of initial and intermediate compounds

$(NH_3OH)Nd(SO_4)_2 \cdot 2H_2O$				$NH_4Nd_3(SO_4)_5$			
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
7.95	6	2.23	6	9.10	6	2.43	3
5.85	10	2.22	6	8.80	10	2.39	3
5.40	2	2.18	6	8.50	6	2.28	4
5.22	2	2.16	5	6.30	9	2.25	3
5.15	8	2.13	1	5.95	3	2.24	3
4.95	8	2.12	2	5.50	3	2.23	2
3.49	10	2.07	1	5.15	8	2.20	1
3.46	8	2.04	1	4.95	2	2.16	2
3.44	8	2.02	3	4.80	3	2.15	1
3.23	3	1.879	5	4.60	2	2.11	1
3.21	3	1.868	5	4.35	4	2.09	1
3.20	3	1.860	2	4.25	4	2.06	1
3.15	9	1.840	2	4.05	3	2.04	2
3.10	2	1.834	2	3.89	4	1.980	2
3.09	1	1.820	4	3.80	4	1.945	4
3.08	1	1.813	3	3.56	4	1.920	3
2.99	8	1.808	3	3.50	1	1.870	2
2.90	4	1.790	4	3.44	6	1.850	1
2.85	6	1.750	4	3.38	6	1.820	3
2.83	6	1.740	5	3.30	4		
2.80	4	1.693	4	3.23	7		
2.71	4	1.680	1	3.18	8		
2.64	3			3.16	8		
2.60	5			3.10	2		
2.48	7			3.02	6		
2.46	7			2.96	1		
2.44	3			2.83	5		
2.40	4			2.75	7		
2.34	1			2.69	5		
2.33	1			2.66	5		
2.31	3			2.60	2		
2.30	3			2.54	3		
2.27	6			2.47	1		

Infrared spectra were measured with a Perkin—Elmer 521 grating spectrometer (4000—250 cm^{-1}). Crystallographic powder spectra were obtained with a Guinier—de Wolff camera using CuK$_\alpha$ radiation.

Results and discussion

The thermal decomposition of $(NH_3OH)Nd(SO_4)_2 \cdot 2H_2O$ (Fig. 1) begins at about 150° with the loss of water. The dehydration, with an endothermic DTA peak at 198°, overlaps with the next stage, where, roughly speaking, the hydroxylammonium sulfate part of the complex decomposes. The decomposition is similar to that of pure $(NH_3OH)_2SO_4$ [3]. It begins with the exothermal disproportionation of hydroxylammonium to ammonium and nitrogen (sharp DTA peak at 238°), and continues with the evaporation of H_2SO_4 (endothermic peak at 255°). The formation of the NH_4^+ ion was also proved by IR-spectroscopy. Part of the IR spectra of the initial compound and of the intermediate phase with a mass loss of 15.8%, obtained by isothermal heating at 160°, are shown in Fig. 2. A strong band at 1420 cm^{-1} and a shoulder at 1430 cm^{-1} can be assigned to NH_4^+ deformation. The corresponding equation could be:

$$3\,(NH_3OH)Nd(SO_4)_2 = NH_4Nd_3(SO_4)_5 + SO_3 + N_2 + 4\,H_2O$$

The theoretical weight loss for the decomposition of the dihydrate to ammonium neodymium sulfate is 23.6%, as compared to the obtained value of 23.0%.

The range of thermal stability of the intermediate compound is large enough for the phase to be isolated. The X-ray powder pattern is different from those of $(NH_4)_2SO_4$ and $Nd_2(SO_4)_3$, showing the phase to be unique. Hydroxylammonium bands are completely absent from the IR spectrum (Fig. 2); only a strong deformation band of NH_4^+ remains.

In the last step ammonium sulfate is lost, yielding $Nd_2(SO_4)_3$, as proved by the X-ray powder pattern. The experimental and calculated total weight losses are 29.00 and 29.05%, respectively.

References

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